

# Sunlight and Iron(III)-Induced Photochemical Production of Dissolved Gaseous Mercury in Freshwater

HONG ZHANG<sup>\*,†,‡</sup> AND  
STEVE E. LINDBERG<sup>†</sup>

*Environmental Sciences Division (ESD),  
Oak Ridge National Laboratory (ORNL),  
P.O. Box 2008, Oak Ridge, Tennessee 37831-6038, and  
Oak Ridge Associated Universities (ORAU),  
P.O. Box 117, Oak Ridge, Tennessee 37831-0117*

Mechanistic understanding of sunlight-induced natural processes for production of dissolved gaseous mercury (DGM) in freshwaters has remained limited, and few direct field tests of the mechanistic hypotheses are available. We exposed ferric iron salt-spiked fresh surface lake water (Whitefish Bay, Lake Superior, MI) in Teflon bottles and pond water (Oak Ridge, TN) in quartz bottles to sunlight in the field to infer if sunlight and Fe(III)-induced photochemical production of DGM could mechanistically contribute partly to natural photochemical production of DGM in freshwaters. We found that exposure of freshwater spiked with fresh Fe(III) (~5 or 10  $\mu$ M) to sunlight led to repeatable, significantly larger increases in DGM production (e.g., 380% in 1 h, 420% in 2 h, and 470% in 4 h for Whitefish Bay water) than exposure without the spike (e.g., 200% in 6 h). DGM increased with increasing exposure time and then often appeared to approach a steady state in the tests. Higher Fe(III) spike levels resulted in the same, or even less, DGM production. Storage of the water with or without Fe(III) spike in the dark after sunlight exposure led to significant, apparently first-order, decreases in DGM. These phenomena were hypothetically attributed to sunlight-induced photochemical production of highly reducing organic free radicals through photolysis of Fe(III)–organic acid coordination compounds and subsequent reduction of Hg(II) to Hg(0) by the organic free radicals; the reduction was also accompanied by dark oxidation of Hg(0) by photochemically originated oxidants (e.g.,  $\cdot$ OH). This study suggests that sunlight and Fe(III)-induced photochemical reduction of Hg(II) could be one of the mechanisms responsible for natural photochemical production of DGM in freshwaters and that Fe species may be influential in mediating Hg chemodynamics and its subsequent toxicity in aquatic ecosystems.

## Introduction

The past decade or more saw discoveries of mercury (Hg) in fish of remote lakes and watersheds in the North America

(e.g., the Everglades, FL; the Great Lakes) and Europe, where local or regional Hg sources were scarce. This has led to many studies focused on these waters (1–11). Further research suggests that the more recent Hg occurrences result from atmospheric deposition of Hg from anthropogenic and natural sources through long-distance atmospheric transport (10–12). Once deposited in natural waters, Hg undergoes an aquatic redox cycling between oxidized Hg, Hg(II), and elemental Hg, Hg(0). Among the Hg(II) pool is toxic, bioaccumulative methylated Hg [ $\text{CH}_3\text{Hg}^+$ ,  $(\text{CH}_3)_2\text{Hg}$ ] and species such as inorganic Hg(II), which can be methylated, while Hg(0) dominates dissolved gaseous mercury (DGM) in freshwater (7, 10), which is subject to evasion back to the atmosphere (6). Mason et al. (13) estimated that the evasion could globally add more than 2000 tons of Hg to the atmosphere annually. Quantifying DGM dynamics and revealing its physicochemical mechanisms thus can vastly benefit our understanding and prediction of aquatic Hg chemodynamics and its subsequent toxicity.

Diel changes of DGM that track solar radiation (typically, highest DGM levels around noon and lowest during night) have been observed in natural freshwaters, e.g., the Everglades, FL (3, 14, 15) and Lake Superior, MI (16, 17). These findings implicate an intrinsic role of sunlight in controlling aquatic DGM dynamics. Recent field sunlight incubations of northern lake waters in Teflon bottles further suggest natural production of DGM through sunlight-induced photochemical reduction of Hg(II) in freshwater (18–20). This is of significance for aquatic Hg biogeochemical cycling and its environmental impacts because the competition of this sunlight-driven pathway for Hg(II) substrate with the methylation pathway would reduce Hg toxic hazards in local aquatic ecosystems through removal of Hg(II) as a result of its reduction to Hg(0) and its subsequent evasion (6, 7). Yet, despite increasing numbers of observations of sunlight-induced aquatic production of DGM in both northern and southern aquatic systems (16, 21), mechanistic understanding of the phenomena has remained limited.

A variety of abiotic, photochemical processes could hypothetically be responsible (18–20, 22, 23). These could be photosensitized, dissolved organic carbon (DOC)-assisted reduction of Hg(II) (22), DOC and dissolved oxygen-assisted reduction of Hg(II) (24), or direct photolysis of Hg(II)–organic acid coordination compounds (25–27). Biotic transformations may also act a part (28, 29). Despite laboratory simulation studies of these processes (24–27, 30), however, field evidences of their possible occurrence in natural waters and the knowledge of their effects on aquatic Hg chemodynamics are lacking or inconclusive.

Ferric iron, Fe(III), is highly photochemically reactive in aqueous media (31). Its role in mediating photochemical redox cycling of heavy metals in natural aqueous systems is well-established (31–33). Photochemical reduction of heavy metal ions [e.g., Cr(VI) (34)] by highly reducing organic free radicals, produced through photolysis of Fe(III)–organic acid coordination compounds caused by electron-transfer absorption of photons, has been implicated to be one of the most important mechanisms of the redox cycling (35). We therefore considered that the same mechanism may also act in the observed sunlight-induced photochemical production of DGM in natural freshwaters (23). This hypothesis is of significance because natural organic substances and Fe are commonly present in freshwaters. Yet, to our knowledge, this link between Fe and aquatic Hg photochemodynamics has received little exploration, although it has been studied in simulated atmospheric droplet systems (30).

\* Corresponding author phone: (865)574-7365; fax: (865)576-8646; e-mail: 2HZ@ornl.gov.

<sup>†</sup> Oak Ridge National Laboratory.

<sup>‡</sup> Oak Ridge Associated Universities.

**TABLE 1. Basic Chemical Characteristics of the Water of Whitefish Bay, MI**

	pH <sup>a</sup>	DOC <sup>a,b</sup> (mg L <sup>-1</sup> )	Fe filtered <sup>a,c</sup> (μg L <sup>-1</sup> )	total Hg <sup>d,e</sup> (ng L <sup>-1</sup> )	dissolved Hg <sup>d,e</sup> (ng L <sup>-1</sup> )	DGM <sup>e</sup> (pg L <sup>-1</sup> )
mean	8.0	2.4	16	1.7	0.5	29
SD	0.1	1	16	0.7	0.4	12
n	20	4	3	3	3	14

<sup>a</sup> Water samples were taken in 1997 and 1998. Data are provided by the Water Chemistry Program, University of Wisconsin (Shafer and Hoffmann, personal communication). <sup>b</sup> 2 μm filtered. <sup>c</sup> 0.4 μm filtered. <sup>d</sup> Data are provided by the Air Quality Laboratory, University of Michigan. <sup>e</sup> Nearshore surface water samples taken in June 1998.

We report here our attempt to test this hypothesis in the field by exposing natural freshwater spiked with Fe(III) salt to sunlight. Our primary tests were done using the fresh lake water from Whitefish Bay in Lake Superior, MI, where significant diel trends in DGM dynamics were previously observed (16) and where we recently completed studies of both DGM trends and soil Hg emission (17, 36). Additional tests were conducted with quartz bottles using the freshwater of a pond at Oak Ridge, TN. The main objectives of this study were to infer if sunlight and Fe(III)-induced photochemical production of DGM could mechanistically contribute in part to the observed natural photochemical production of DGM in freshwaters and to shed light on our further elaborate laboratory investigation of this mechanism under controlled conditions. Implications of the findings of this study for aquatic Hg chemodynamics are also discussed.

## Experimental Section

**Field Test Site.** Whitefish Bay is located in the eastern end of Lake Superior in the Great Lakes. Previous studies show that the nearby Tahquamenon River, the major tributary of Whitefish Bay, was both DOC- and Fe-enriched (e.g., DOC = ~6.8–23.7 mg L<sup>-1</sup>, dissolved Fe = ~3.5–5.9 μM) (Shafer and Hoffman, personal communication). Table 1 lists the basic chemical characteristics of the water of Whitefish Bay. Nearshore surface water samples were collected ~10 m from the shoreline of Whitefish Bay in Paradise, MI (~46.55° N, 85.05° W).

**Procedures for Water Sampling and Field Tests.** Fresh surface lake water samples were collected using a glass container (10% HNO<sub>3</sub> washed, prebaked at ~500 °C for 4–6 h) and then transferred to transparent Teflon bottles [Nalgene, Ø8.5 cm × 17.5 cm, 1 L, 70–80% UV transmission (19); 10% HNO<sub>3</sub> soaked overnight, rinsed with Milli-Q deionized distilled water (MQDDW), stored in MQDDW]. Each Teflon bottle was first rinsed with fresh lake water 3 times before filling. To investigate the photochemical effect of Fe(III), the bottles were first spiked with 0.5 or 1.0 mL of 5 or 10 mM Fe(III) solution of sulfate salt [lower photosensitivity than NO<sub>3</sub><sup>-</sup>, lower affinity for Hg(II) than Cl<sup>-</sup>, Mallinckrodt, AR, freshly made for each test with MQDDW immediately before the bottles were filled], and then they were completely hand-filled with fresh lake water (final Fe(III) spike levels in the bottles = ~5 or 10 μM) and cap-sealed with no internal headspace. In a few cases, 1 mL of 50 mM sodium oxalate solution was also spiked to test the effect of organic acids. Immediately after filling, the bottles were partly submerged in a water bath in a place nearby to begin sunlight exposure. The bottles were so placed that they received the maximum sunlight. The temperature of the water tested was roughly kept at ~20 °C through water replacement. Some tested bottles were kept in a dark cooler at ~20 °C as dark controls.

Similar procedures were followed in the supporting tests using quartz bottles and fresh surface water from a small

freshwater pond near our lab at ORNL (14 × 50 m<sup>2</sup>, pH = ~8, TOC = ~3.1 mg L<sup>-1</sup>, total Fe = ~2.3 μM, total Hg = ~2.7 ng L<sup>-1</sup>, easily reducible Hg = ~0.35 ng L<sup>-1</sup>). The quartz bottles (ORNL-manufactured, Ø 8 cm × 20 cm, 1 L, 25 cm high overall, 10% HNO<sub>3</sub> washed, prebaked at ~500 °C for ~5 h) were rinsed, Fe(III)-spiked, filled with 1 L of freshwater, stopper-sealed with a headspace (hs) <110 mL, and then exposed to sunlight. The potential DGM loss to this small headspace is estimated to be < 4% at ~25 °C [ $H_{25^{\circ}C} = (H_{hs}/V_{hs})/(H_{water}/V_{water}) = \sim 0.32$  (16)]. Given the nature of this field study, our tests both in Michigan and Tennessee were often inevitably subject to natural fluctuations in solar radiation and in temperature of the tested water, with the former being more substantial than the latter.

**DGM Determination.** DGM measurements were made immediately after a water collection for determination of initial DGM or after a required sunlight exposure. If not possible occasionally, the samples were kept in a dark cooler and analyzed as soon as possible. For the tests with Teflon bottles, each water sample to be tested was first carefully transferred to a state-of-the-art DGM purging bottle (DGM-PB) made of glass (acid-washed, prebaked at ~500 °C for ~5 h). DGM was then immediately measured, in situ, with a Tekran 2537A automated Hg vapor analyzer (sampling time = 5 min, sampling flow = 1.5 L min<sup>-1</sup>) through the DGM-PB following a method developed by Lindberg et al. (14) and Vette (16). Briefly, the DGM-PB has a removable glass purger insert with an inlet attached to an iodated charcoal trap and an outlet connected to the Hg analyzer. Zero (Hg-free) air, obtained by pulling ambient air through the charcoal trap, was pulled into the DGM-PB directly by the Hg analyzer to purge and deliver the DGM for its determination. For the tests with quartz bottles, immediately after completion of a photoexposure, a similar purger insert as described above was quickly put directly into the quartz testing bottle for DGM determination. The quartz bottle thus served first for exposure test and then as a DGM-PB. This eliminated possible DGM loss caused by water transfer. All DGM measurements were performed indoor, with the DGM-PB and each quartz bottle kept in the dark (covered with aluminum foil for DGM-PB or kept inside a dark box for quartz bottles).

A complete DGM determination on these waters generally required ~30–40 min of purging (3 or 4 DGM samples followed by 3 or 4 system blank checks). Usually, ~70–80% of the total DGM was purged out during the first DGM sampling, and after 3 or 4 samples, the Hg levels dropped to reach a steady state, which was regarded as the system blank (14, 17). The DGM content (pg L<sup>-1</sup>) was calculated by  $DGM = (\sum Hg \text{ purged} - \sum \text{system blank})/V_{water}$ , where the number of the readings for purged Hg is equal to the number of the readings for the blank. In this study with only one Tekran Hg analyzer available, the repetition of similar sunlight exposure tests at different times was preferred to simultaneous analytical replication because of the time required for each DGM analysis (~30–40 min) and possible decay of DGM during dark storage.

**Other Measurements.** Global solar radiation ( $R_g$ ) was monitored near the exposure site periodically during each field test with a Li-Cor photometer. The data on DOC and dissolved Fe of the lake water were provided by the Water Chemistry Program, University of Wisconsin (Shafer and Hoffman, personal communication). Total and filtered Hg in the lake water was analyzed by the Air Quality Laboratory, University of Michigan (16, 37, 38). Chemical analyses of the pond water were performed at ORNL; TOC was analyzed by a Shimadzu TOC analyzer; total Fe was analyzed by AA; total Hg and easily reducible Hg (SnCl<sub>2</sub>-reduced without initial oxidation by BrCl) were analyzed using a protocol adapted from EPA Method 1631 (39).

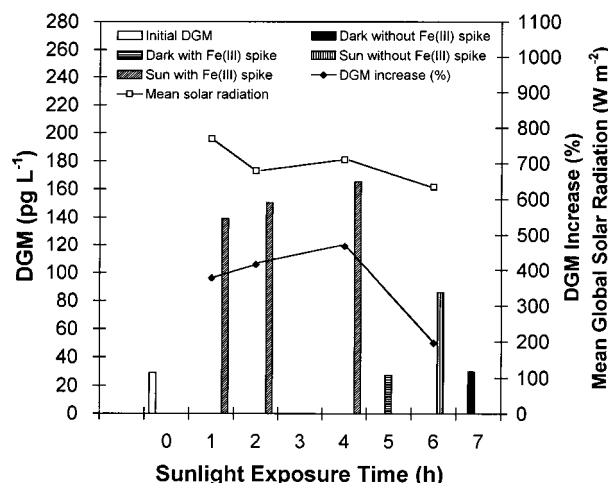


FIGURE 1. Typical demonstration of Fe(III)-enhanced sunlight-induced photochemical production of DGM in fresh nearshore surface water from Whitefish Bay at Paradise, MI [Teflon bottle, Fe(III) spiked = 10  $\mu\text{M}$ ,  $T_{\text{sun-exposure}}$  =  $\sim 20^\circ\text{C}$ , 6/27/98].

## Results and Discussion

**Sunlight-Induced Production of DGM without Fe(III) Spike.** Both the previous and present studies showed that DGM in Whitefish Bay exhibited typical diel trends following solar radiation (16, 17). This implies occurrence of sunlight-mediated photochemical production of DGM in the lake water. Exposing fresh lake water from Whitefish Bay to sunlight in this study, we also observed significant DGM increases (Figure 1, Table 2). As an example, the DGM concentrations increased from 51 to 67  $\text{pg L}^{-1}$  ( $\sim 31\%$ ) in sunlight for 3 h, and in another case increased from 29 to 86  $\text{pg L}^{-1}$  ( $\sim 200\%$ ) for 6 h. These observations suggest that photochemical formation of DGM is an important contributing process for DGM production in the lake.

**Effect of Fe(III) on Sunlight-Induced Production of DGM in Freshwater.** Exposing fresh lake water from Whitefish Bay spiked with fresh Fe(III) to sunlight led to significantly more DGM increases than exposure without Fe(III) spike (Figure 1, Table 2). As typically shown in Figure 1, DGM levels rose from 29 to 140 (380%, 1 h sunlight), to 150 (420%, 2 h), and to 170  $\text{pg L}^{-1}$  (470%, 4 h) as compared to the case without Fe(III) spike, 86  $\text{pg L}^{-1}$  (200%, 6 h). The Fe(III)-induced DGM increases were further verified by more similar tests during this study (Table 2).

We observed no DGM increases in the dark storage of the fresh lake water with Fe(III) spike (Figure 1, Table 2). This implies that the Fe(III)-enhanced reduction of Hg(II) to DGM required sunlight. This also indicates the absence of any inadvertent introduction of elemental Hg into the tested bottles along with the Fe(III) spike. The total and easily reducible Hg levels of the spiked Fe(III) solutions (spike level  $\leq 1 \text{ mL}$ ) were  $\sim 37 \pm 14$  and  $\sim 15 \pm 7 \text{ pg mL}^{-1}$ , respectively, which cannot account for the observed substantial DGM increases. This is also consistent with our observations of little increase in DGM production with increasing Fe(III) spike level (see below).

One uncertainty regarding interpretation of our observed Fe(III)-enhanced photochemical production of DGM may arise from the use of Teflon bottles in the field tests. The walls of Teflon bottles are known to be able to absorb gaseous Hg(0) (21), and its removal can be difficult unless the bottles were sufficiently baked at high temperatures (e.g.,  $500^\circ\text{C}$ ), which is impossible for Teflon material. The absorbed Hg could diffuse out of the wall into solution upon sunlight exposure (Lindberg, unpublished data; 21). Plausibly, the observed DGM increases could result partly from the

contribution of the sunlight-desorbed Hg(0) (or residual effect, probably significant in the cases where the bottles were previously exposed to high levels of DGM). Incidentally, thick-walled Teflon bottles also receive incomplete sunlight penetration ( $\sim 80\%$ ). To resolve this uncertainty as well as to further study sunlight and Fe(III)-induced photochemical production of DGM in freshwater, we used quartz bottles to perform sunlight exposure tests similar to those conducted at Whitefish Bay and additional supporting tests using freshwater from a freshwater pond at ORNL. The results of these experiments confirmed our observations of the Fe(III)-enhanced photochemical production of DGM in natural freshwater (Figure 2, Table 3). As typically shown in Figure 2, the same trends in DGM increases were found with the quartz bottles for the pond water as with the Teflon bottles for the lake water (Figure 1). The same phenomenon was also recently observed in Florida using freshwater from the Everglades (Zhang et al., manuscript in preparation).

Organic acid (oxalate, a model carboxylic acid) was also spiked in fresh lake water to test the effect of dissolved organic substances in photochemical production of DGM. We found DGM increases of magnitudes similar to those without oxalate spike (Table 2). This seems to suggest that the natural organic substances already present in the lake water were probably sufficient for the photochemical production of DGM via the Fe(III)-involved mechanism, although oxalate is well-known for its photochemical function in the presence of Fe(III) (30, 35).

The kinetics of the sunlight and Fe(III)-enhanced photochemical production of DGM observed in this study is summarized in Table 4. It appears that the data can be fit equally well by both first- and second-order kinetics. However, given the questionable assumption required for the fit by second-order kinetics (i.e.,  $[\text{Hg(II)}]_0 = [\text{reductant}]_0$ ), the first-order kinetics may be more acceptable. The values of first-order rate constant ( $k$ ) and half-life ( $t_{1/2}$ ) from this study average approximately at  $0.2 \text{ h}^{-1}$  and 6 h for the lake water and  $0.1 \text{ h}^{-1}$  and 9 h for the pond water, respectively. Given the nature of this study (e.g., under field conditions, especially, varying solar radiation), these kinetic values are probably more meaningful in a qualitative sense.

**Effect of Spiked Fe(III) Level.** We found that increasing Fe(III) spike levels from 10 to 30 and to 50  $\mu\text{M}$  led to less DGM production in sunlight exposure of the lake water (Figure 3). After 2 h of exposure, 25  $\text{pg L}^{-1}$  of DGM was found with a spike of 30  $\mu\text{M}$  Fe(III) and 30  $\text{pg L}^{-1}$  of DGM was found with 50  $\mu\text{M}$  Fe(III) as compared to 166  $\text{pg L}^{-1}$  with 10  $\mu\text{M}$  Fe(III) (initial DGM = 20  $\text{pg L}^{-1}$ ). Indoor UV exposure (germicidal lamp,  $\sim 254 \text{ nm}$ ) of the lake water led to similar findings (Figure 3). Exposing the pond water in quartz bottles to sunlight, we also found that the DGM produced at higher Fe(III) spike levels was close to that at lower levels. For example, in a 2.5-h sunlight exposure, 109  $\text{pg L}^{-1}$  of DGM was found with 2.5  $\mu\text{M}$  Fe(III) and 122  $\text{pg L}^{-1}$  of DGM was found with 5  $\mu\text{M}$  Fe(III) as compared to 106  $\text{pg L}^{-1}$  with 1  $\mu\text{M}$  Fe(III) (initial DGM = 32  $\text{pg L}^{-1}$ ). Thus, higher Fe(III) levels seemed to cause no more or even less net photochemical production of DGM as in these tests.

**Oxidation of DGM in the Dark.** We observed that storage of fresh lake water in the dark frequently caused DGM decreases, e.g., from 47 to 34  $\text{pg L}^{-1}$  for 5 h and from 42 to 37  $\text{pg L}^{-1}$  for 5.5 h in separate tests at Whitefish Bay (Figure 1, Table 2). Similar DGM decreases in dark storage were also seen elsewhere, e.g., in lake water (19), in the water of the Everglades (14, 21), and in seawater (40). These DGM decreases over time indicate that DGM must be removed via some mechanisms. These could be dark oxidation of DGM back to Hg(II), adsorption of DGM by suspended particles, or absorption of DGM into the Teflon bottle wall.



TABLE 2. Fe(III)-Enhanced Sunlight-Induced Photochemical Production of DGM in Fresh Lake Water from Whitefish Bay, MI<sup>a</sup>

date	time	light	mean $R_g^b$ ( $W\ m^{-2}$ )	Fe(III) spike ( $\mu M$ )	$t_{sun-exposure}$ (h)	DGM ( $\mu g\ L^{-1}$ )	increase <sup>c</sup> (%)	increase rate <sup>d</sup> ( $\mu g\ L^{-1}\ h^{-1}$ )
6/22/98	1330					51 <sup>e</sup>		
	1330–1430	dark	-	0	1	47	-8	-4
	1330–1630	sun	-	0	3	67	31	5
6/23/98	940					47 <sup>e</sup>		
	1000–1500	dark		0	5	34	-28	-3
	1000–1100	sun	170 $\pm$ 26	10	1	180	280	130
	1000–1230	sun	220 $\pm$ 110	10	2.5	210	350	65
	1000–1400	sun	540 $\pm$ 420	10	4	350	650	76
6/23/98	1600					42 <sup>e</sup>		
	1600–2130	dark	-	0	5.5	37	-12	-1
	1600–1700	sun	650 $\pm$ 35	10 <sup>f</sup>	1	79	88	37
	1600–1900	sun	510 $\pm$ 160	10 <sup>f</sup>	3	100	140	19
	1600–2000	sun	400 $\pm$ 240	10 <sup>f</sup>	4	220	420	45

<sup>a</sup> Results of field tests with Teflon bottles. Water temperature during sunlight exposure =  $\sim 20^\circ C$ . <sup>b</sup> Global solar radiation. <sup>c</sup> Increase (%) = [(treatment - initial DGM)/initial DGM]  $\times$  100. <sup>d</sup> Increase rate = (treatment - initial DGM)/ $t_{sun-exposure}$ . <sup>e</sup> Initial DGM. <sup>f</sup> Spiked additionally with 50  $\mu M$  oxalate.

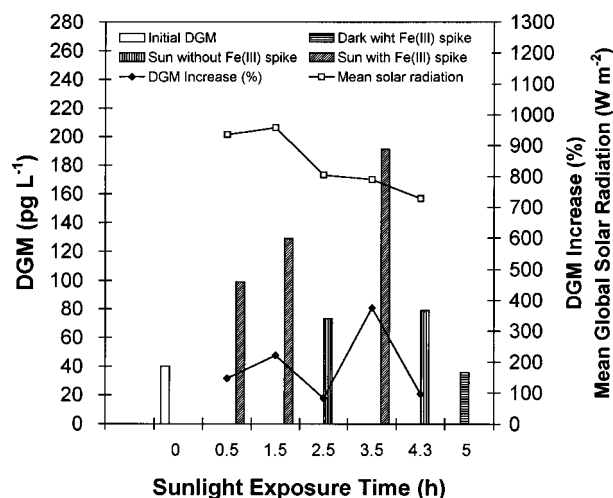
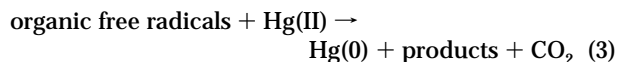
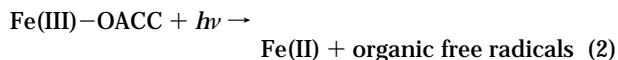
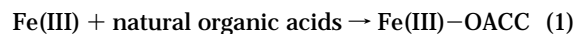


FIGURE 2. Typical demonstration of Fe(III)-enhanced sunlight-induced photochemical production of DGM in fresh surface water from a freshwater pond at Oak Ridge, TN [quartz bottle, Fe(III) spiked = 5  $\mu M$ ,  $T_{sun-exposure}$  =  $\sim 30^\circ C$ , 4/27/00].

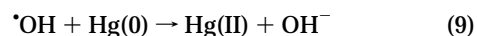
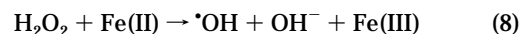
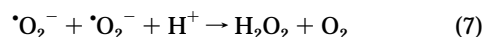
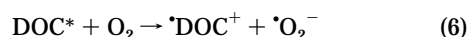
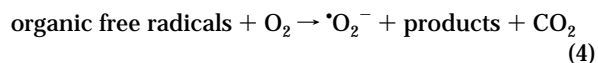
To further investigate the dark oxidation of Hg(0) and reveal the origin of the oxidants, we exposed the pond water with or without Fe(III) spike in quartz bottles to sunlight first and then monitored the subsequent changes over time of DGM concentrations of the same water placed in the dark immediately after the photoexposure. We found significant DGM decreases during the subsequent dark storage, and longer storage led to further DGM decreases, both with and without Fe(III) spike (Figure 4). The DGM decreases in the dark exhibited apparent first-order kinetics (with Fe(III) spike,  $k = 0.2\ h^{-1}$ ,  $t_{1/2} = 4\ h$ ,  $R^2 = 0.97$  for  $\log[DGM]$  vs  $t$ ; without Fe(III) spike,  $k = 0.3\ h^{-1}$ ,  $t_{1/2} = 2\ h$ ,  $R^2 = 0.98$ ). This behavior is similar to that observed by Lindberg et al. in the Everglades, FL ( $k = 0.1\text{--}0.6\ h^{-1}$ ) (14), and by Amyot et al. in seawater ( $k = \sim 0.1\ h^{-1}$ ) (40). Since the suspended particles in the water had settled out and also had reached steady state with the DGM in the quartz bottles during the sunlight exposure, the DGM decreases can be reasonably attributed to its dark oxidation by some oxidants. These were probably photochemically produced in the presence of natural organic substances and Fe(III) during the photoexposure. These observations thus seem to implicate a redox cycling of Hg characterized by reduction in sunlight and oxidation in the dark, probably occurring simultaneously and both originated photochemically. This would explain observations of de-

creasing DGM at night and generally low values at first light (14, 21).

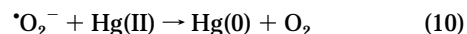
**Hypothetical Mechanism for Sunlight and Fe(III)-Induced Photochemical Redox Cycling of Hg in Freshwater.** Our current hypothesis on the abiotic mechanism to explain the observed effects of Fe(III) includes (i) sunlight-induced photochemical production of highly reducing organic free radicals through photolysis of Fe(III)-organic acid coordination compounds [Fe(III)-OACC] and subsequent reduction of Hg(II) by the organic free radicals (23):



and (ii) dark oxidation of Hg(0) by photochemically originated oxidants (23, 35, 41):



Also possibly, the reduction of Hg(II) might be catalyzed by dissolved oxygen (DO) (24):



where  $\cdot O_2^-$  is a superoxide free radical. In addition to reaction 8,  $\cdot OH$  might also be produced in natural water by direct photolysis of DOC (42):



Reduction of Hg(II) with Fe(III) spike proceeded much faster than without Fe(III) spike thus largely because the

TABLE 3. Fe(III)-Enhanced Sunlight-Induced Photochemical Production of DGM in Fresh Water from a Pond at Oak Ridge, TN<sup>a</sup>

date	time	light	mean $R_g^b$ ( $W\ m^{-2}$ )	Fe(III) spike ( $\mu M$ )	$t_{\text{sun-exposure}}$ (h)	DGM ( $\mu g\ L^{-1}$ )	increase <sup>c</sup> (%)	increase rate <sup>d</sup> ( $\mu g\ L^{-1}\ h^{-1}$ )
11/11/1999	1200					51 <sup>e</sup>		
	1200–1700	dark		10	5	28	–45	–5
	1220–1520	sun	500 ± 150	0	3	46	–10	–2
	1220–1320	sun	390 ± 190	10	1	61	20	10
	1220–1420	sun	580 ± 86	10	2	89	75	19
11/17/1999	1220–1620	sun	410 ± 220	10	4	100	96	12
	1100					14 <sup>e</sup>		
	1120–1450	dark		10	3.5	14	0	0
	1120–1240	sun	690 ± 150	0	1.3	36	160	17
	1120–1150	sun	760 ± 97	10	0.5	75	440	120
11/18/1999	1120–1320	sun	640 ± 210	10	2	90	540	38
	1020			5		46 <sup>e</sup>		
	1040–1210	sun	550 ± 40	0	1.5	51	11	3
	1040–1310	sun	520 ± 31	0	2.5	63	37	7
	1040–1340	sun	500 ± 52	0	3	53	15	2
	1040–1240	sun	540 ± 13	5	2	120	160	37

<sup>a</sup> Results of field tests with quartz bottles. Water temperature during sunlight exposure: ~29 °C on 11/11/99, ~18 °C on 11/17/99, and ~21 °C on 11/18/99. <sup>b</sup> Global solar radiation. <sup>c</sup> Increase (%) = [(treatment - initial DGM)/initial DGM] × 100. <sup>d</sup> Increase rate = (treatment - initial DGM)/ $t_{\text{sun-exposure}}$ . <sup>e</sup> Initial DGM.

TABLE 4. Summary of Kinetics of Fe(III)-Enhanced Sunlight-Induced Photochemical Production of DGM in Freshwater Tested in this Study

date	water	initial DGM ( $\mu g\ L^{-1}$ )	Fe(III) spike ( $\mu M$ )	mean $R_g^c$ ( $W\ m^{-2}$ )	assuming first-order <sup>a</sup>			assuming second-order <sup>b</sup>		
					$R^2$	$k\ (h^{-1})$	$t_{1/2}\ (h)$	$R^2$	$k\ (M^{-1}\ s^{-1})$	$t_{1/2}\ (h)$
6/23/1998	Whitefish Bay	47	10	310	0.92	0.3	3	0.86	$6 \times 10^7$	2
6/23/1998	Whitefish Bay	42	10 <sup>d</sup>	520	0.76	0.1	6	0.72	$2 \times 10^7$	7
6/27/1998	Whitefish Bay	29	10	700	0.66	0.07	10	0.69	$1 \times 10^7$	10
11/11/1999	ORNL pond	51	10	470	0.93	0.05	14	0.94	$1 \times 10^7$	14
4/27/2000	ORNL pond	40	5	840	0.97	0.2	4	0.99	$4 \times 10^7$	4
5/17/2000	ORNL pond	5	5	290	0.92	0.07	10	0.92	$1 \times 10^7$	14

<sup>a</sup> Regression of  $\log([Hg(II)]_0 - [DGM])$  vs  $t$ ,  $n = 4$ , assuming  $[Hg(II)]_0 = 500\ \mu g\ L^{-1}$  for nearshore surface water from Whitefish Bay and  $[Hg(II)]_0 = 350\ \mu g\ L^{-1}$  for surface water from a pond at ORNL. <sup>b</sup> Regression of  $1/([Hg(II)]_0 - [DGM])$  vs  $t$ ,  $n = 4$ , assuming  $[Hg(II)]_0 = 500\ \mu g\ L^{-1}$  for nearshore surface water from Whitefish Bay and  $[Hg(II)]_0 = 350\ \mu g\ L^{-1}$  for surface water from a pond at ORNL. <sup>c</sup>  $R_g$  = global solar radiation. <sup>d</sup> Spiked additionally with  $50\ \mu M$  oxalate.

spiked fresh dissolved Fe(III) led to rapid production of highly reducing organic free radicals in aqueous phase (via reactions 1 and 2) (23, 35), which can rapidly reduce Hg(II) (via reaction 3). Reactions 1 and 2 could also occur to Fe(III) species in solid phase [e.g., Fe(III)(OH)<sub>n</sub> polymers, iron oxides] (30, 43), although production of organic free radicals involving Fe(III) species in amorphous or solid phase is slower than in the presence of soluble Fe(III) species (43). Hence, Fe(III)-assisted photochemical production of DGM may not necessarily require dissolved Fe(III) species. Because of the presence of natural organic acids in freshwaters, a fraction of Fe(III) is expected to coordinate with these acids and thus becomes soluble and photochemically reactive. As the levels of both DOC and dissolved Fe are fairly significant in the waters tested (Whitefish Bay: DOC = ~2.4 mg L<sup>-1</sup>, Fe = ~0.3  $\mu M$ ; pond: TOC = ~3.1 mg L<sup>-1</sup>, Fe = ~2.3  $\mu M$ ), we consider that a certain fraction of the Fe(III) pool was photochemically reactive and available for mediating photochemical production of DGM following the above mechanism in these natural waters.

Reactions 4–9 and 11 describe a mechanism for dark oxidation of Hg(0) in the presence of Fe(III) and DOC by photochemically originated oxidants. H<sub>2</sub>O<sub>2</sub> could be photochemically produced in the presence of Fe(III)–OACC in sunlight through reactions 4 and 7 (35) or by photosensitization of DOC through reactions 5–7 (41). The generated H<sub>2</sub>O<sub>2</sub> could then cause oxidation of Hg(0) through reaction 9 by highly oxidizing hydroxyl free radical (\*OH) produced through reaction 8, the Fenton reaction (44). This has been shown to play a significant role in redox cycling of heavy

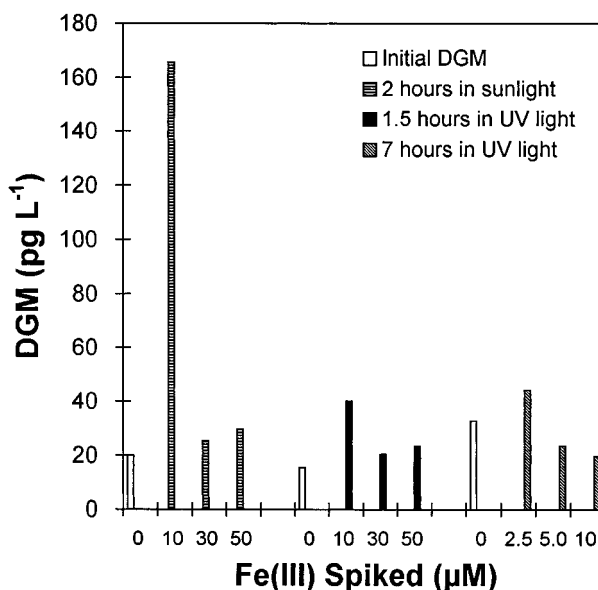


FIGURE 3. Effect of Fe(III) spike level on Fe(III)-enhanced sunlight-induced photochemical production of DGM in fresh nearshore surface water from Whitefish Bay at Paradise, MI [Teflon bottle;  $T_{\text{sun-exposure}} = \sim 20\ ^\circ C$ , mean  $R_g = 770\ W\ m^{-2}$ ;  $T_{\text{UV-exposure}} = \sim 18\ ^\circ C$ , mean  $R_g = \sim 5\ W\ m^{-2}$ ; 6/29/98].

metals (31, 32, 35, 44) and regarded as an important source of \*OH in natural aqueous media (31, 44). Oxidation of Hg(0)

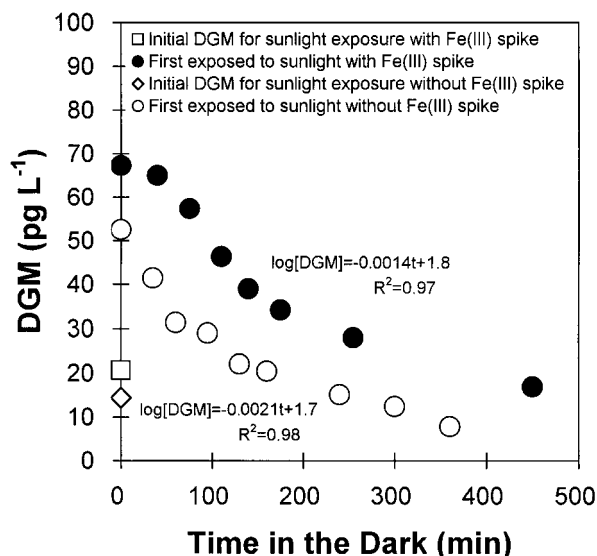


FIGURE 4. Decreases in DGM concentrations in the dark after sunlight exposure of fresh surface water from a freshwater pond at Oak Ridge, TN, with Fe(III) spike [quartz bottle, Fe(III) spiked =  $5 \mu\text{M}$ ,  $t_{\text{sun-exposure}} = 1 \text{ h}$ , mean  $R_g = 810 \text{ W m}^{-2}$ ,  $T_{\text{sun-exposure}} = \sim 29\text{--}30^\circ\text{C}$ ; assuming first-order kinetics,  $k = 0.2 \text{ h}^{-1}$ ,  $t_{1/2} = 4 \text{ h}$ ; assuming second-order kinetics,  $k = 3.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,  $5/18/00$ ] and without Fe(III) spike [quartz bottle,  $t_{\text{sun-exposure}} = 1 \text{ h}$ , mean  $R_g = 810 \text{ W m}^{-2}$ ,  $T_{\text{sun-exposure}} = \sim 26\text{--}27^\circ\text{C}$ ; assuming first-order kinetics,  $k = 0.3 \text{ h}^{-1}$ ,  $t_{1/2} = 2 \text{ h}$ ; assuming second-order kinetics,  $k = 8.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,  $5/19/00$ ].

by  $\cdot\text{OH}$  appears to be an important oxidation pathway for  $\text{Hg}(0)$  in natural waters (25, 30).

To further test the hypothesis of the dark oxidation of  $\text{Hg}(0)$  by photochemically originated oxidants, we first exposed the pond water spiked with Fe(III) to sunlight of different intensity and then followed the DGM concentrations of the same water samples during their subsequent dark storage. Our preliminary tests showed that DGM concentrations decreased faster in the samples preexposed to sunlight of higher intensity than in those to sunlight of lower intensity (Table 5, at mean  $R_g = 930 \text{ W m}^{-2}$ ,  $k = 0.3 \text{ h}^{-1}$ ,  $t_{1/2} = 3 \text{ h}$ , at mean  $R_g = 690 \text{ W m}^{-2}$ ,  $k = 0.2 \text{ h}^{-1}$ ,  $t_{1/2} = 4 \text{ h}$ ). This observation appears to support the hypothesis, although further tests are needed in this regard. The kinetics of the dark oxidation found in this study seem to suggest that the oxidants apparently had a fairly long lifetime, which is consistent with the hypothesis that the acting oxidant ( $\cdot\text{OH}$ ) originates from relatively stable  $\text{H}_2\text{O}_2$  through the Fenton reaction.

The decreased DGM production at higher Fe(III) spike levels mentioned before (Figure 3) thus could be due to both the oxidation during dark storage and the oxidation during sunlight exposure, each resulting from more photochemical production of oxidants at higher Fe(III) levels. The water freshly collected in daylight could also be rich in photochemically produced oxidants, which probably were responsible for the observed loss of DGM in freshwater during its dark storage. The lack of the effect of oxalate may also be due to its promotion of DGM oxidation.

**Implications for Hg Chemodynamics in Natural Freshwaters.** In the presence of Fe(III) and organic substances and in sunlight, aquatic Hg appears to photochemically cycle between  $\text{Hg}(\text{II})$  and  $\text{Hg}(0)$  as described above. The cycling is steered jointly by light intensity, amount of  $\text{Hg}(\text{II})$  and  $\text{Hg}(0)$ , amount and speciation of organic substances, and amount of available photochemically reactive Fe(III) species and perhaps DO. The variation in measured DGM thus points to the direction of the cycling. In a closed system (e.g., a test bottle), the general pattern may be an initial dominant

TABLE 5. Effect of Light Intensity during Sunlight Exposure of Fe(III)-Spiked Fresh Water on Oxidation of DGM in Subsequent Dark Storage of the Same Water<sup>a</sup>

$t_{\text{dark-storage}}$ (h)	mean $R_g = 690 \text{ W m}^{-2b}$			mean $R_g = 930 \text{ W m}^{-2b}$		
	DGM (pg L <sup>-1</sup> )	DGM change <sup>c</sup> (%)	change rate <sup>d</sup> (pg L <sup>-1</sup> h <sup>-1</sup> )	DGM (pg L <sup>-1</sup> )	DGM change <sup>c</sup> (%)	change rate <sup>d</sup> (pg L <sup>-1</sup> h <sup>-1</sup> )
0	45 <sup>e</sup>			52 <sup>e</sup>		
0.7	77 <sup>f</sup>			98 <sup>g</sup>		
1		-13	-14		-36	-35
1.2	63	-18	-12	63	-45	-29
1.5				54	-50	-25
1.8	56	-27	-12	49	-54	-18
2				45		
3						

<sup>a</sup> The tests were conducted using the ORNL pond water spiked with  $5 \mu\text{M}$  Fe(III). <sup>b</sup>  $R_g$  = global solar radiation. At  $R_g = 690 \text{ W m}^{-2}$ , assuming first-order,  $R^2 = 0.99$ ,  $k = 0.2 \text{ h}^{-1}$ ,  $t_{1/2} = 4 \text{ h}$ ; assuming second-order,  $R^2 = 0.99$ ,  $k = 1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . At  $R_g = 930 \text{ W m}^{-2}$ , assuming first-order,  $R^2 = 0.88$ ,  $k = 0.3 \text{ h}^{-1}$ ,  $t_{1/2} = 3 \text{ h}$ ; assuming second-order,  $R^2 = 0.94$ ,  $k = 2.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . <sup>c</sup> DGM change (%) = [(DGM in dark storage - DGM without dark storage)/DGM without dark storage]  $\times 100$ . <sup>d</sup> Change rate = (DGM in dark storage - DGM without dark storage)/ $t_{\text{dark-storage}}$ . <sup>e</sup> Initial DGM. <sup>f</sup> DGM without dark storage immediately after 0.75 h of sunlight exposure at  $T_{\text{sun-exposure}} = \sim 30^\circ\text{C}$  (5/5/00). <sup>g</sup> DGM without dark storage immediately after 1.8 h of sunlight exposure at  $T_{\text{sun-exposure}} = \sim 25^\circ\text{C}$  (5/15/00).

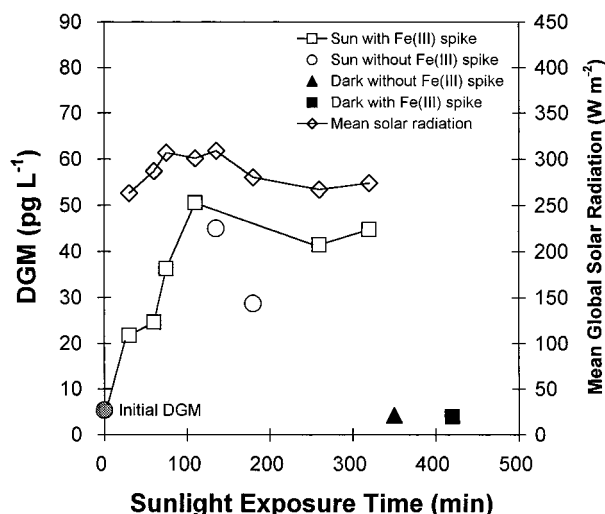


FIGURE 5. Reaction kinetics showing steady state of Fe(III)-enhanced sunlight-induced photochemical production of DGM in fresh surface water from a freshwater pond (Oak Ridge, TN) during sunlight exposure [quartz bottle, Fe(III) spiked =  $5 \mu\text{M}$ ,  $T_{\text{sun-exposure}} = \sim 22\text{--}24^\circ\text{C}$ , 5/17/00].

photochemical reduction of  $\text{Hg}(\text{II})$  via reactions 1–3 followed by significant dark oxidation of the produced  $\text{Hg}(0)$  via reactions 4–9, probably with a steady state finally reached in many cases (e.g., Figure 5). This is consistent with the observation of DGM production plateau in sunlight exposure of fresh lake water without Fe(III) spike (19).

In open aquatic systems (e.g., lakes, ponds), however, the reduction would prevail, especially under windy conditions (3), because of removal of the produced DGM through evasion (4, 6). Yet, the oxidation would be boosted whenever the evasion abates (i.e., more like in the case of a closed system) under various meteorological or atmospheric chemical conditions (e.g., light wind, high airborne Hg levels). As sunlight fades during the day or around sunset, the oxidation would also become intensified, accompanied by a decline in photochemical production of DGM. Subtropical waters might



hold a different poise between reduction of Hg(II) and oxidation of Hg(0) coupled with their different Fe(III)/Fe(II) levels as compared to freshwaters at high latitudes, but further studies are needed along this line (e.g., ref 3). Sunlight intensity thus appears to play a central role in steering photochemical redox cycling between Hg(II) and Hg(0) in the presence of organic substances and Fe(III) species in freshwaters. The sunlight-driven chemical clock thus intrinsically governs aquatic Hg dynamics as manifested by the observed diel trends of DGM in freshwaters.

In aquatic systems deficient in Fe, a natural addition of Fe-containing substances to the systems, e.g., through atmospheric deposition of Fe-containing dusts (e.g., wind-transported Saharan dust or soil dust), could locally perturb the aquatic Hg redox poise (or steady state) and reshape the local aquatic Hg chemodynamics. Artificial introduction of Fe might offer a potential means of reducing local aquatic Hg exposure by removing Hg from the water through photochemical production of DGM and its subsequent evasion. Such a process could represent a net decrease in production of methyl mercury. However, this would obviously be a local "solution" that also contributes to the overall global "problem" (of increased Hg emissions to the atmosphere). Since Fe is an important nutrient for aquatic biota, aquatic biological activities may be indirectly influential to Hg dynamics and toxicity in natural waters through the Fe link.

The major findings of this study, carried out under field conditions, are generally consistent with the hypothesis that sunlight and Fe(III)-induced photochemical production of DGM could be mechanistically responsible in part for natural photochemical production of DGM in freshwaters. We are currently conducting laboratory tests under controlled conditions to further quantify the kinetics and verify the proposed mechanism of sunlight and Fe(III)-induced photochemical redox cycling of Hg in natural freshwater. The influence of air/surface exchange and the effects of amorphous and solid Fe(III) species and dissolved oxygen on the aquatic photochemodynamics of Hg deserve special interest. Quantitative comparison of this mechanism with other photochemical pathways (e.g., aquatic humics-mediated Hg redox) and especially with biotic transformations of Hg in aquatic systems is a salient future research need.

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